Design of Catalysts and Electrocatalysts: From DFT Prediction to Experimental Verification

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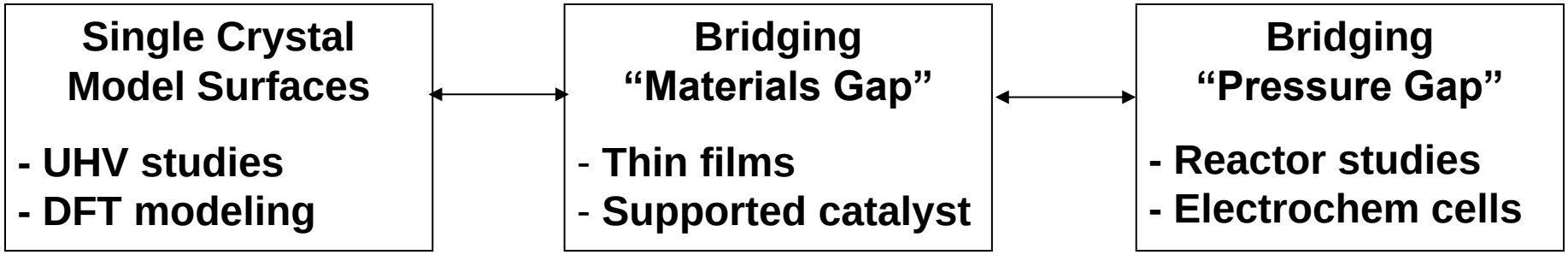
Development of Novel Catalysts

- Supported catalysts:
  - More relevant to commercial catalysts and processes
  - Fast (high throughput) evaluation
  - “Heterogeneous” in electronic and catalytic properties

- Single crystal surfaces:
  - Atomic level understanding from experiments and theory
  - Materials gap: single crystal vs. polycrystalline materials
  - Pressure gap: ultrahigh vacuum (UHV: ~10^{-12} psi)

- Need to bridge “materials gap” and “pressure gap”

From DFT Prediction to Experimental Verification

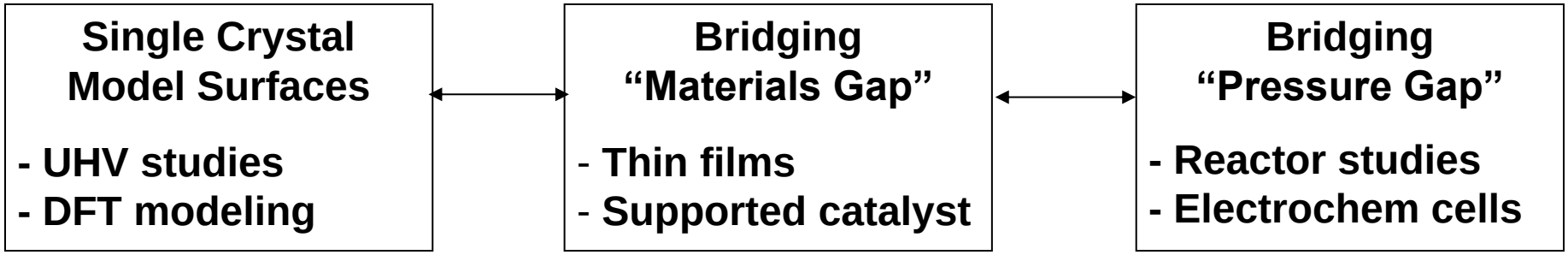


Use DFT to assist catalysts design: (activity, selectivity, stability, cost):

- Binding energy calculations (activity, stability)

- Activation barriers and reaction network (selectivity)

Outline of Presentation



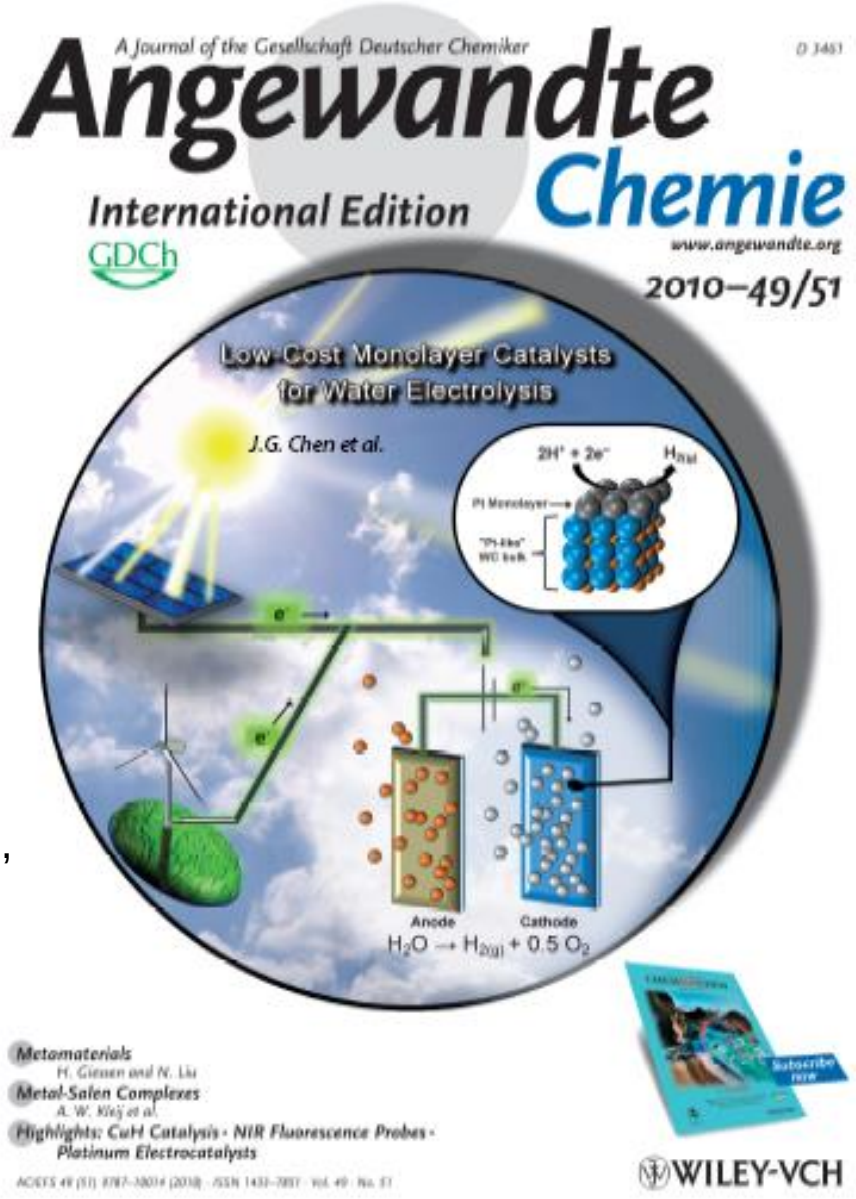
***Examples* of DFT prediction and experimental verification:**

- Correlating hydrogen binding energy (HBE) with water electrolysis activity

- Correlating hydrogen binding energy (HBE) with hydrogenation activity

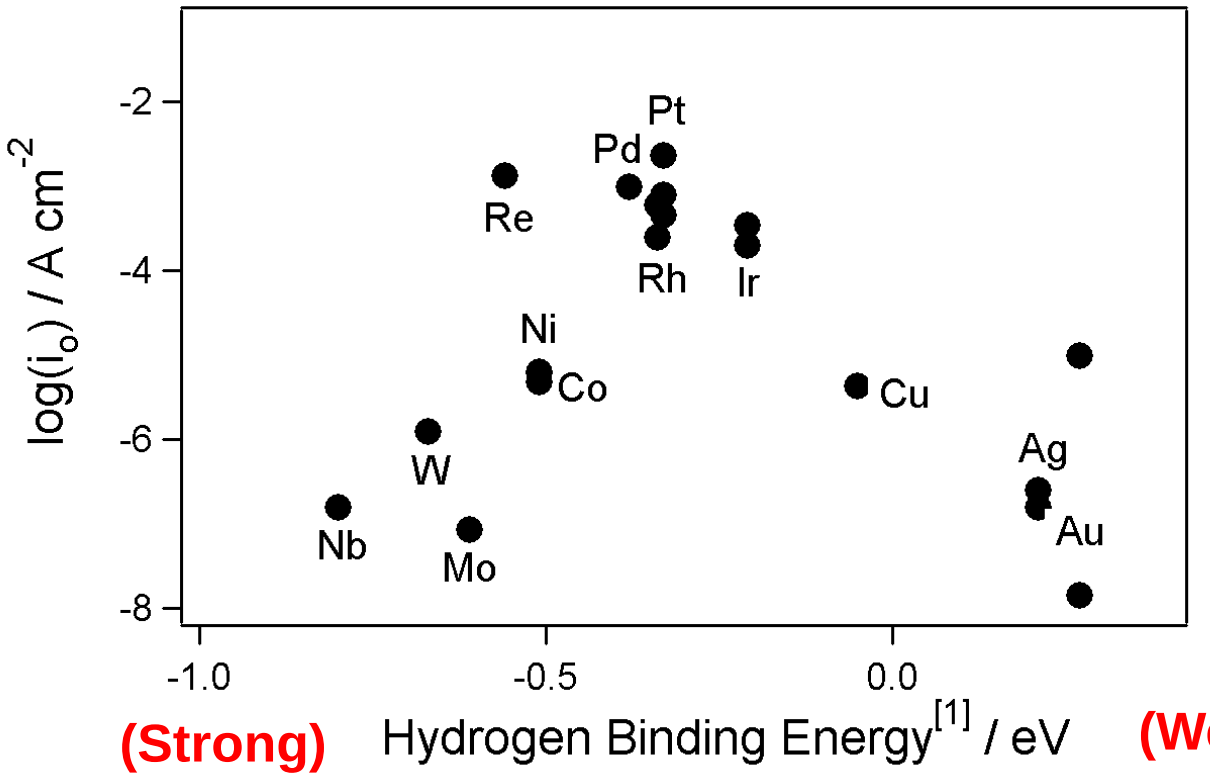
- Correlating activation barrier with hydrogenation selectivity

Correlating HBE with Water Electrolysis Activity



Esposito, Hunt & Chen,
Angew. Chem. Int. Ed.
49 (2010) 9859

HER Activity and Hydrogen Binding Energy (HBE)



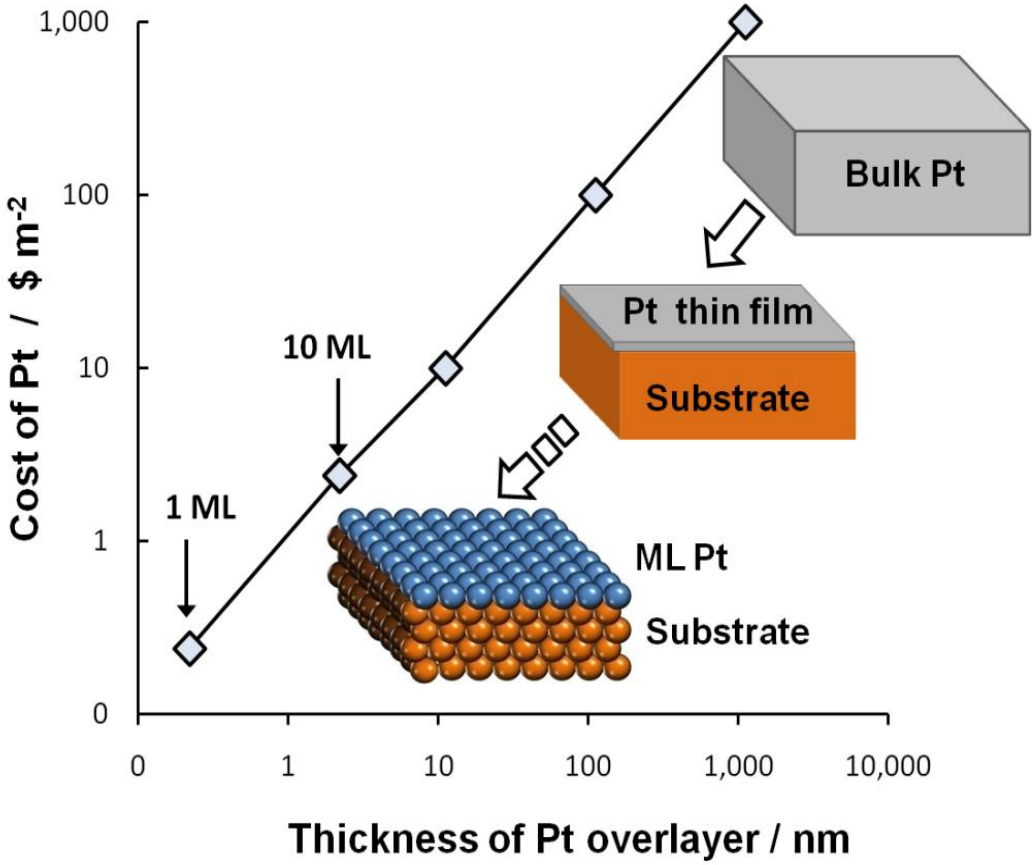
- Classic volcano curve observed for the HER is explained by Sabatier'sPrinciple

$$H^+ + e^- + * \rightarrow H^*$$ (Volmer Step)

$$2H^* \rightarrow H_{2(g)} + 2*$$ (Tafel Step)

[1] Data from: Norskov, Bligaard, Logadottir, Kitchin, Chen, Pandelov, Stimming, J.Electrochem. Soc., 152 (2005) J23-26.

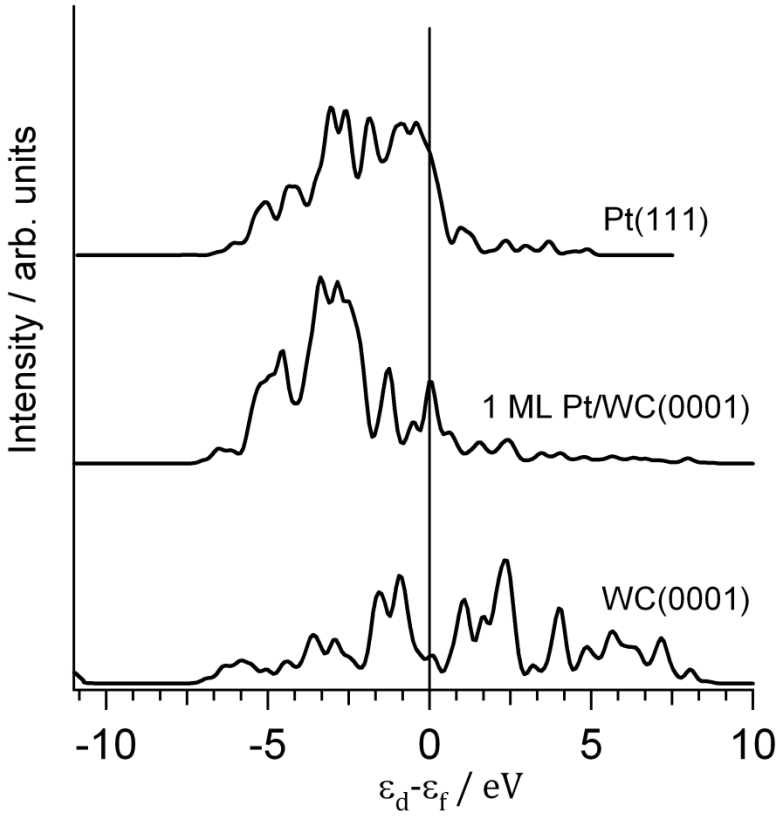
Reduce Pt Loading with Monolayer (ML) Pt



Goal: Supporting ML Pt on Pt-like substrates, such as WC

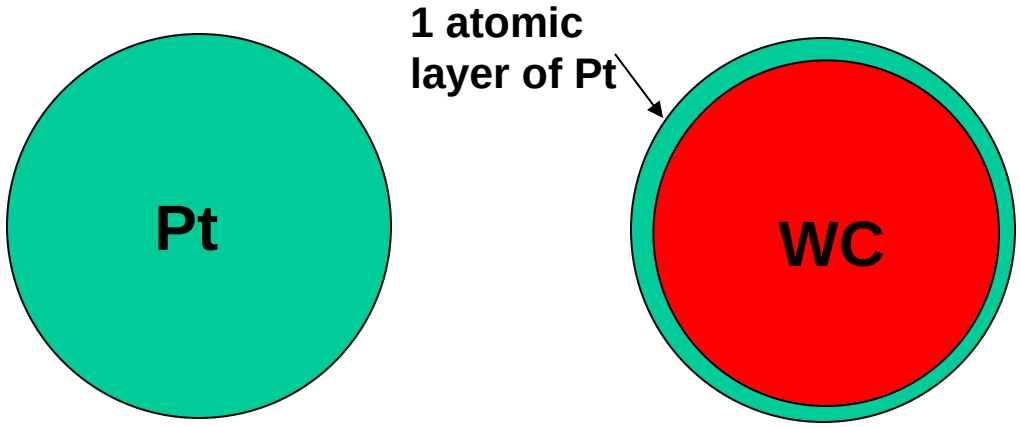
DFT Prediction: Similar HBE Values between Monolayer Pt-WC and Bulk Pt

d-band density of states

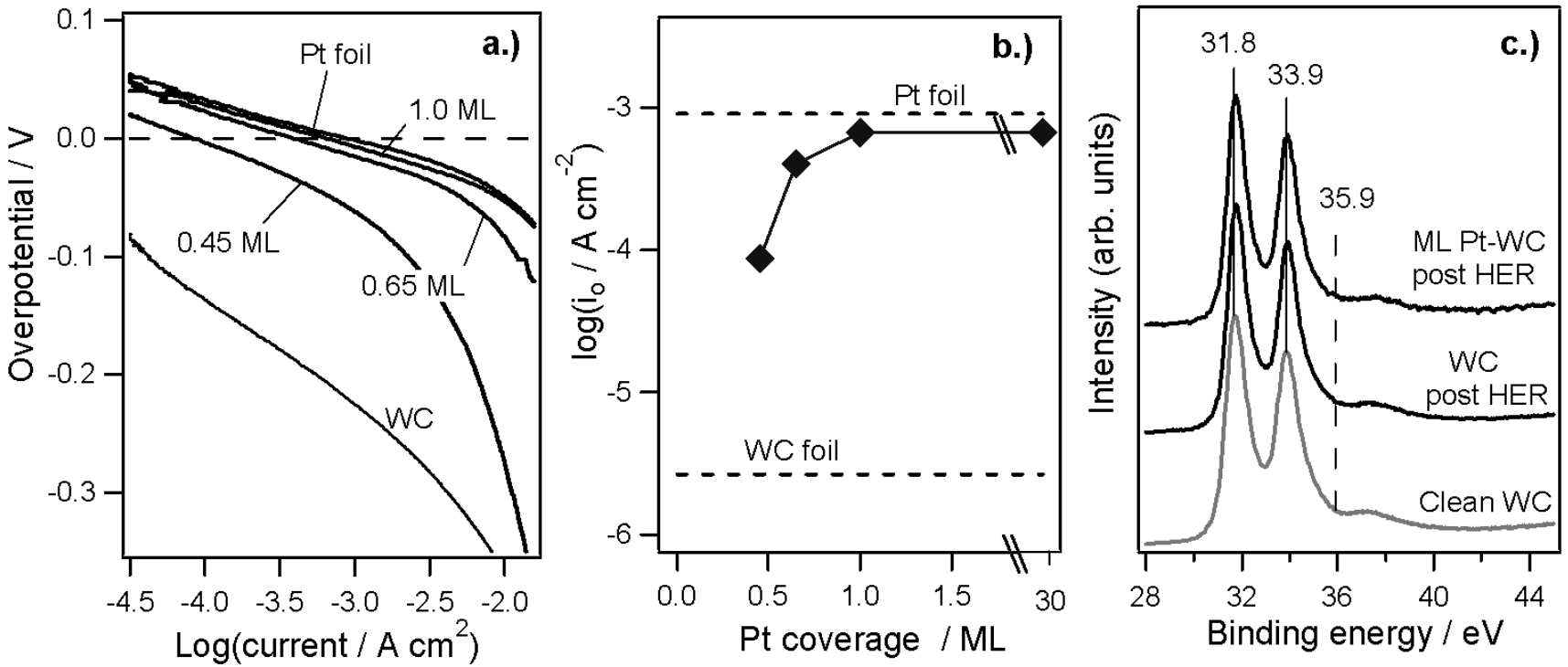


Surface	HBE (eV)
WC(001)	-0.99
Pt(111)	-0.46
1 ML Pt-WC(001)	-0.43

DFT-calculated per-atom hydrogen binding energy (HBE) for WC, Pt, and 1 ML Pt-WC surfaces with a hydrogen coverage of 1/9 ML.



Experimental Verification of Activity and Stability



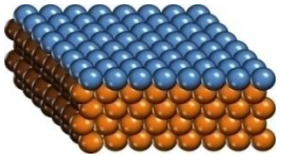
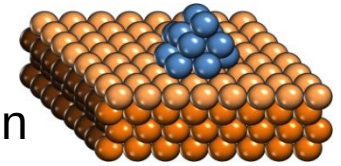
HER Activity of 1 ML Pt/WC approaches to that of Pt foil

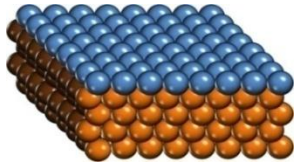
Esposito, Hunt, Birmire & Chen, *Angew. Chem. Int. Ed*. 49 (2010) 9859

DFT Prediction of Stability of Pt/WC and Pt/C

- Use DFT to compare adhesion of Pt atoms to WC and Pt surfaces:

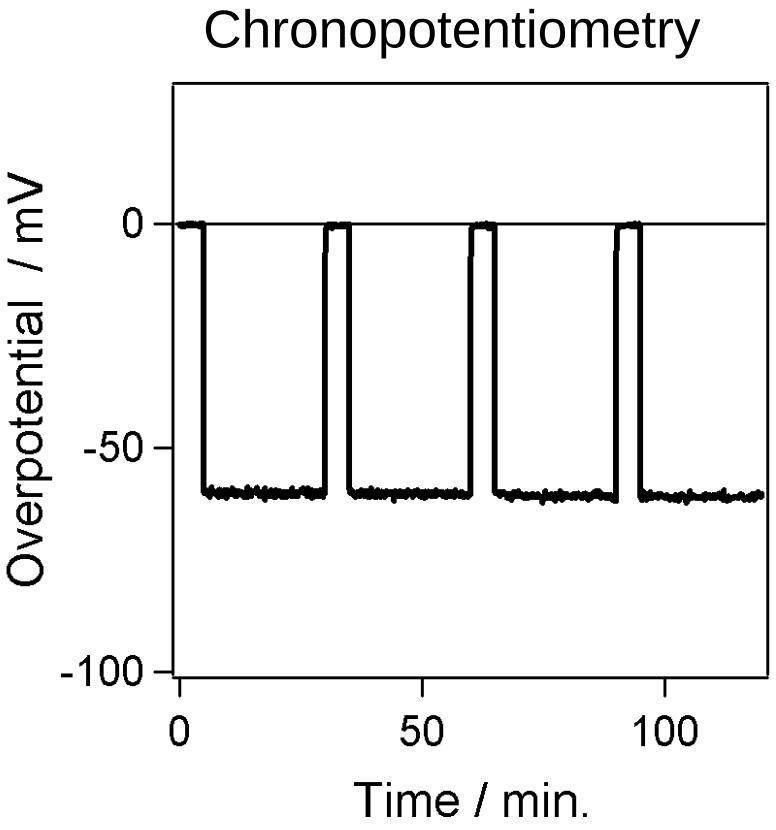
Binding Energy | **Outcome**

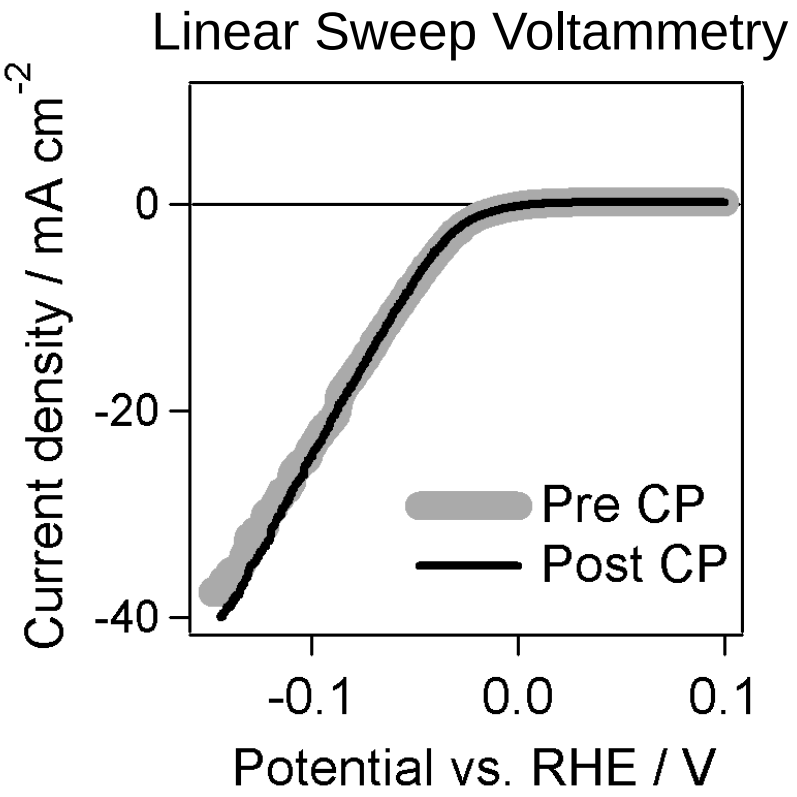
Pt-(Substrate) < Pt-Pt ⇒  Pt migration  Particles favored

Pt-(Substrate) > Pt-Pt ⇒  ML configuration favored

ML surface atoms	Substrate	Binding energy / eV	(M-X^) - (M-M) BE / eV
Pt	Pt(111)	-5.43	0.00
	C(0001)	-4.12	**1.31**
	WC(0001)	-6.59	**-1.16**
	W_2C(0001)	-6.51	-1.08

Experimental Verification of HER Stability

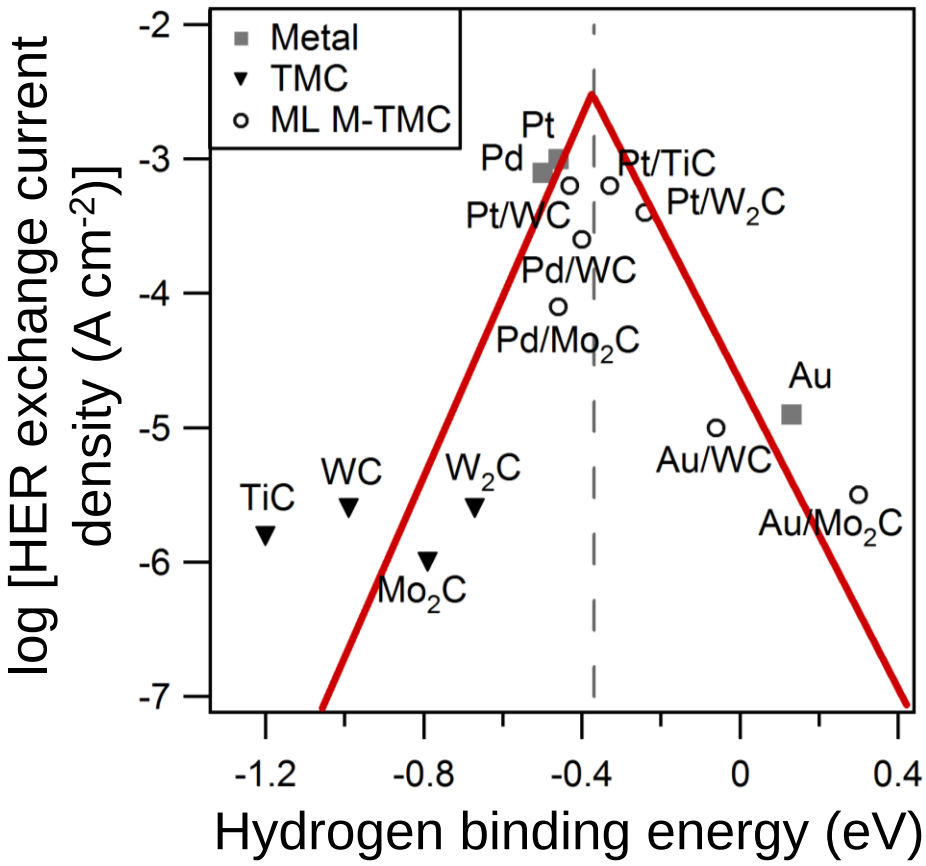




- No change in overpotential observed with time
- No change in LSV before and after CP
- XPS and SEM measurements confirmed stability

Esposito, Hunt & Chen, *J. Am. Chem. Soc.* 134 (2012) 3025

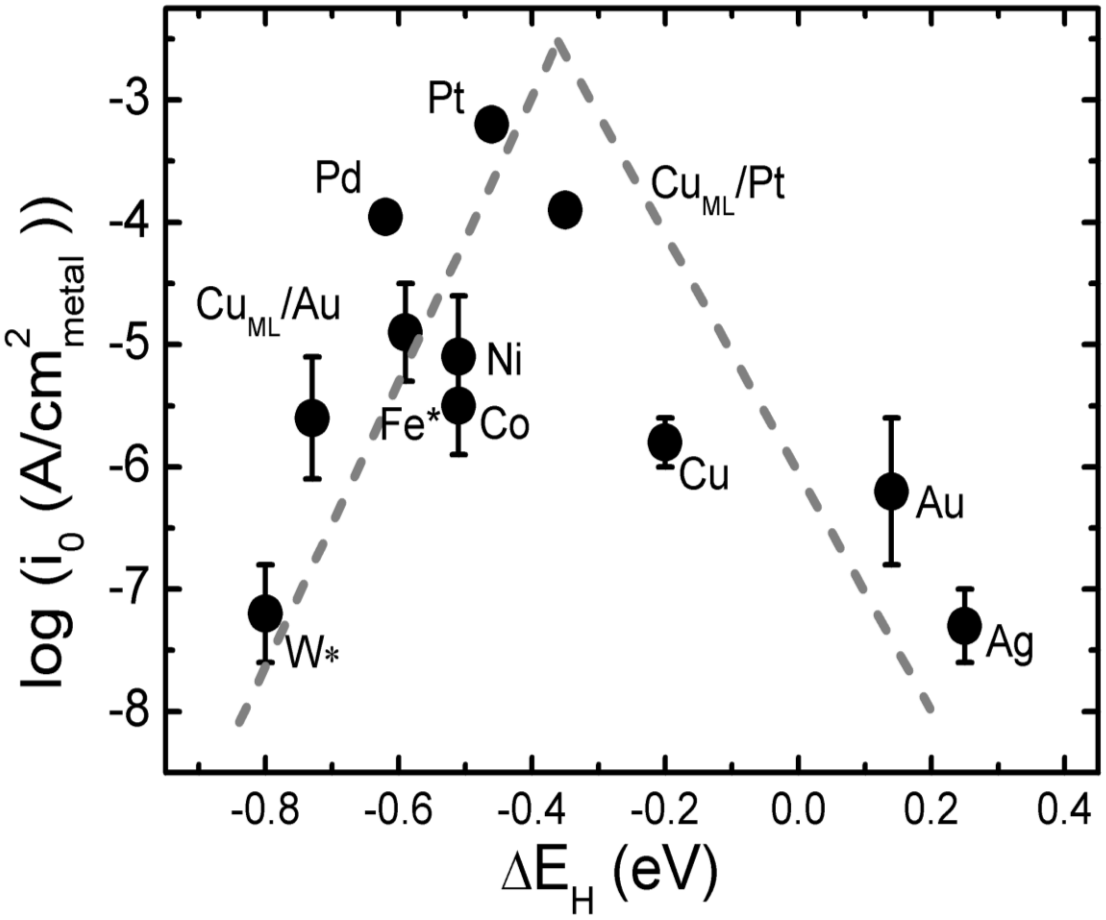
Other ML/TMC Electrocatalysts for HER in Acid



Volcano relationship provides design principles of electrocatalysts

Kimmel , Yang & Chen, *J. Catalysis, 312 (2014) 216*

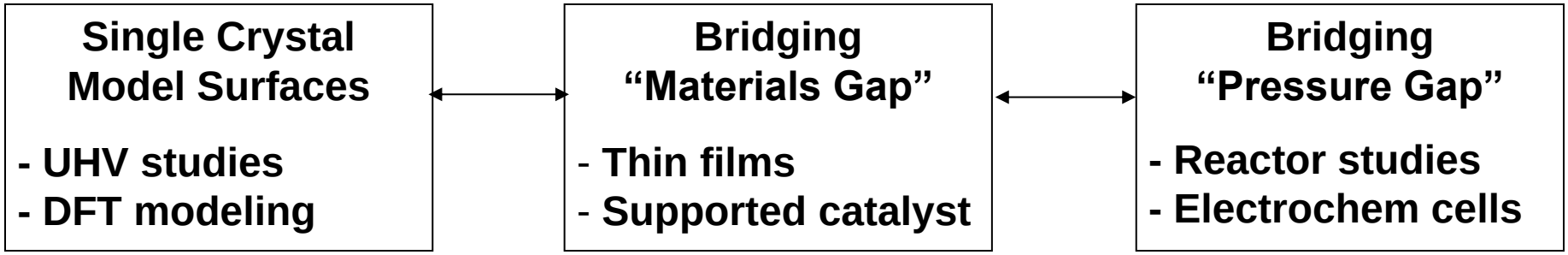
HER Catalysts in Alkaline Environment



Volcano relationship also appears to hold in alkaline electrolyte

Sheng et al. *Energy & Env. Sci*. 6 (2013) 1509

Outline of Presentation



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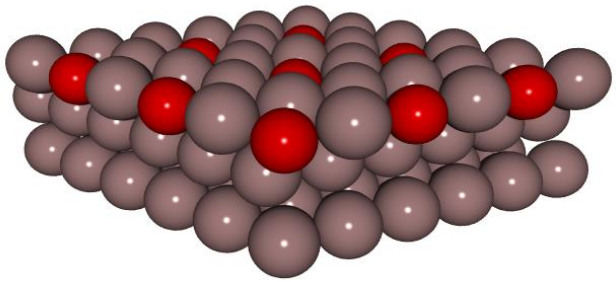
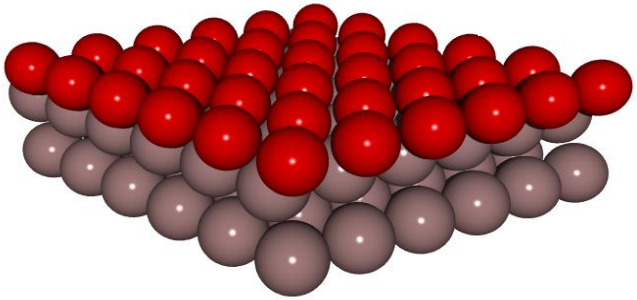
- Correlating hydrogen binding energy (HBE) with hydrogenation activity

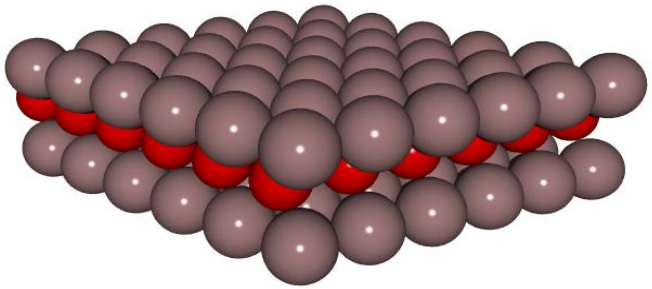
- Correlating activation barrier with hydrogenation selectivity

Monolayer Bimetallic Surfaces

Surface Alloy







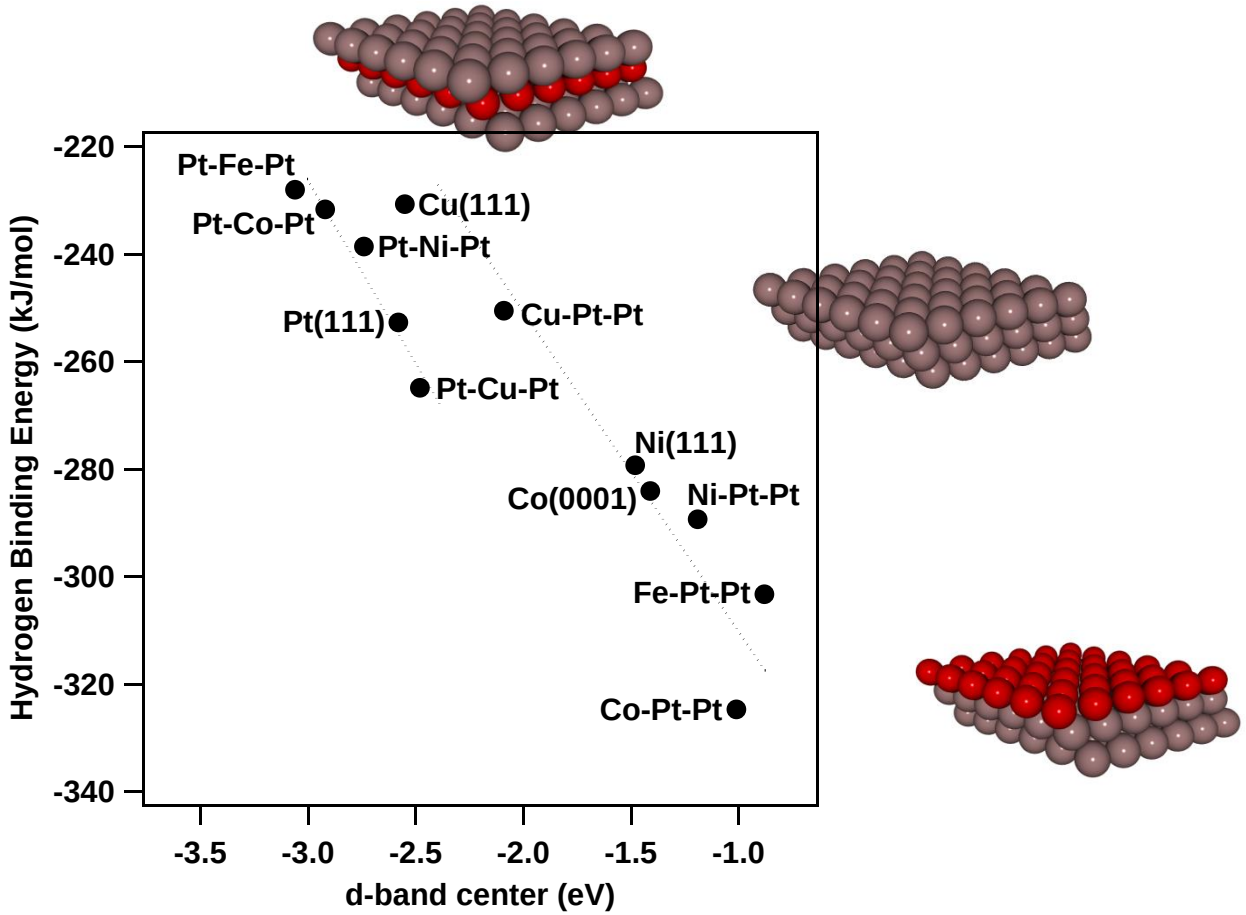
Surface Monolayer

Subsurface Monolayer

Modified surface chemical properties due to:

- –Ligand effect – electronic configuration
- –Compressive and tensile strain - lattice mismatch

DFT Prediction of HBE Values

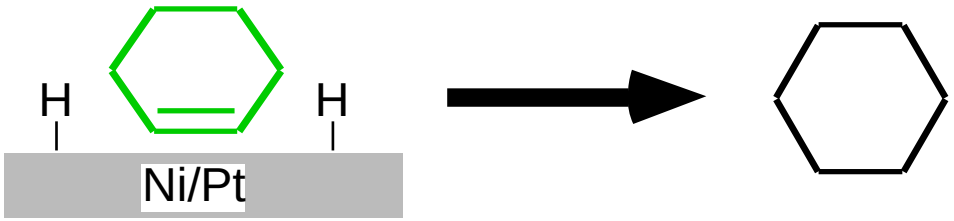


Hydrogen binding energy (HBE) can be controlled by surface structures

Kitchin, Norskov, Barteau & Chen, *Phys. Rev. Lett*. 93 (2004) 156801
Murillo, Goda & Chen, *J. Am. Chem. Soc.* 129 (2007) 7101

Controlling Hydrogenation Activity:
Correlating with Binding Energy

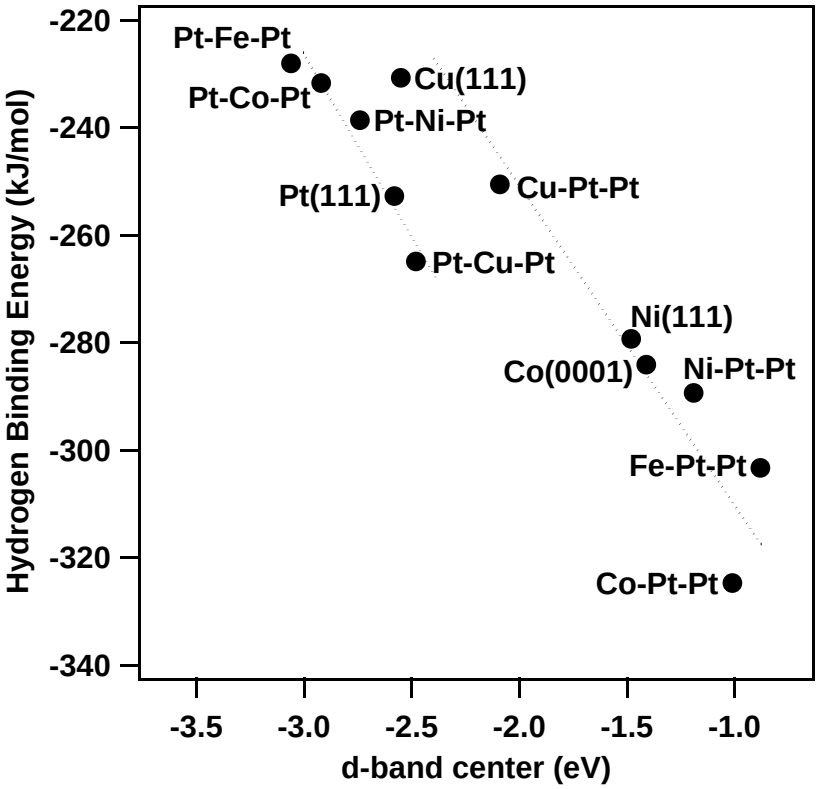
Low-Temperature Cyclohexene Hydrogenation:

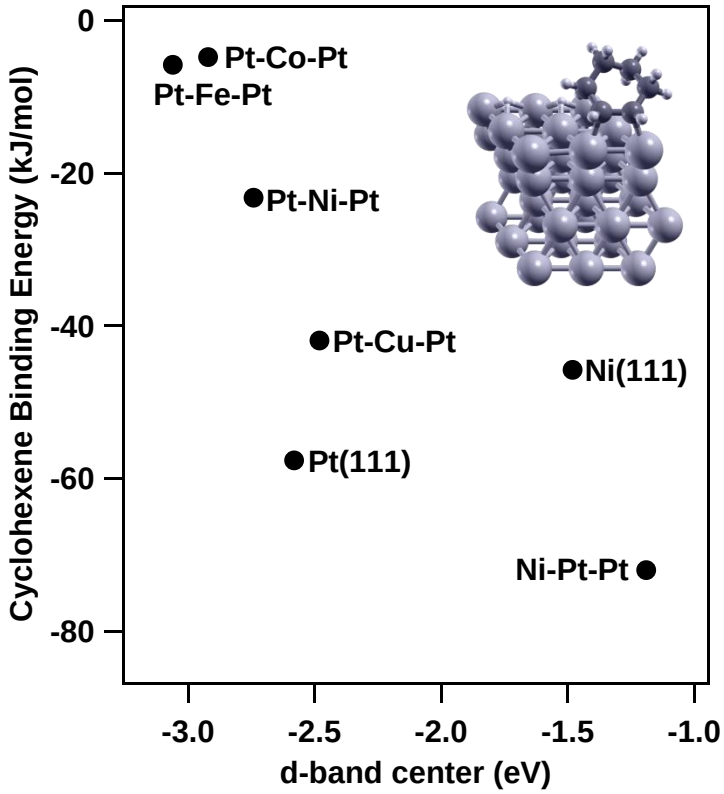


Assumption for Higher Hydrogenation Activity:

- Weakly bonded H atoms
- Weakly bonded cyclohexene

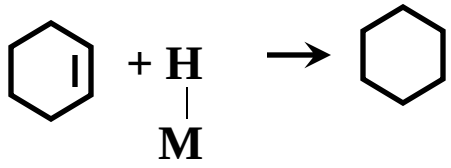
DFT Calculations of Binding Energies of Hydrogen and Cyclohexene

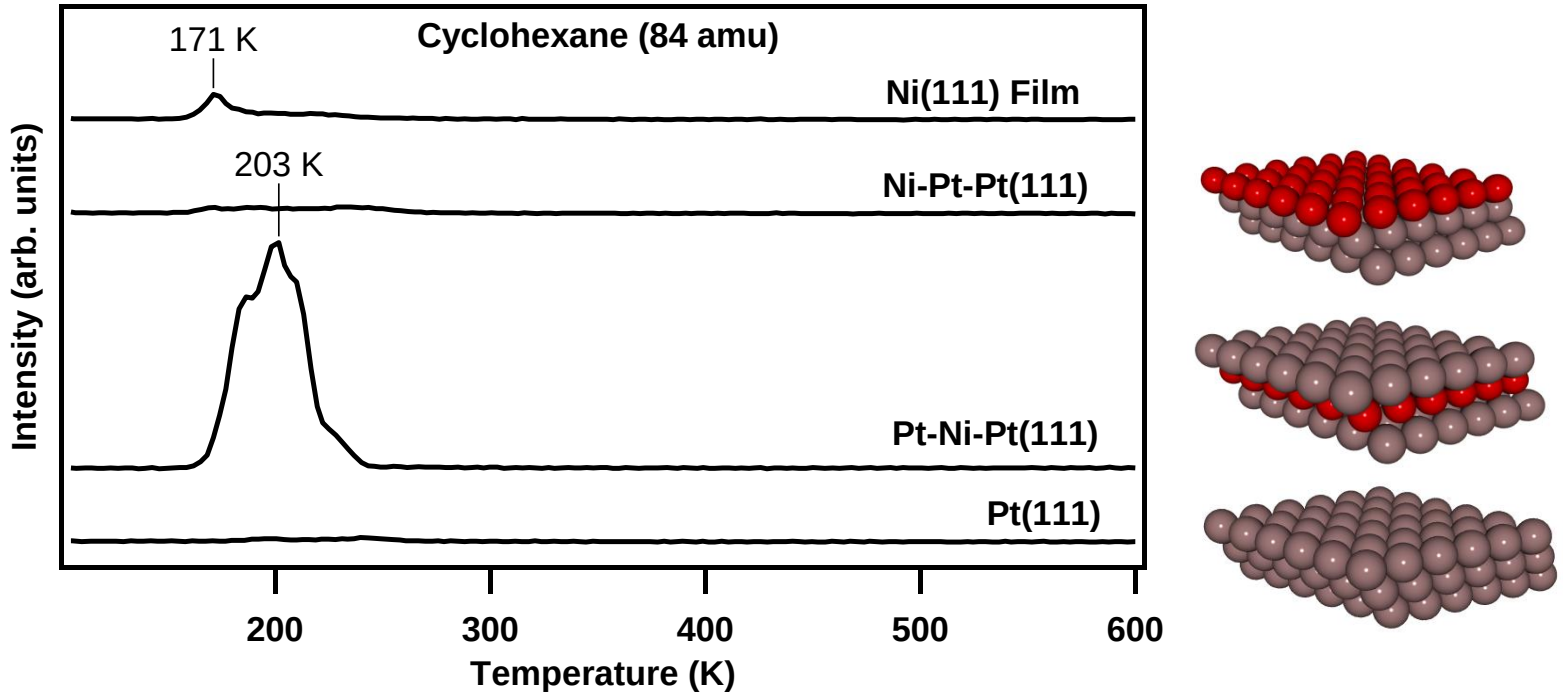




BE values follow the same trend: Ni-Pt(111) > Ni ~ Pt > Pt-Ni-Pt(111)

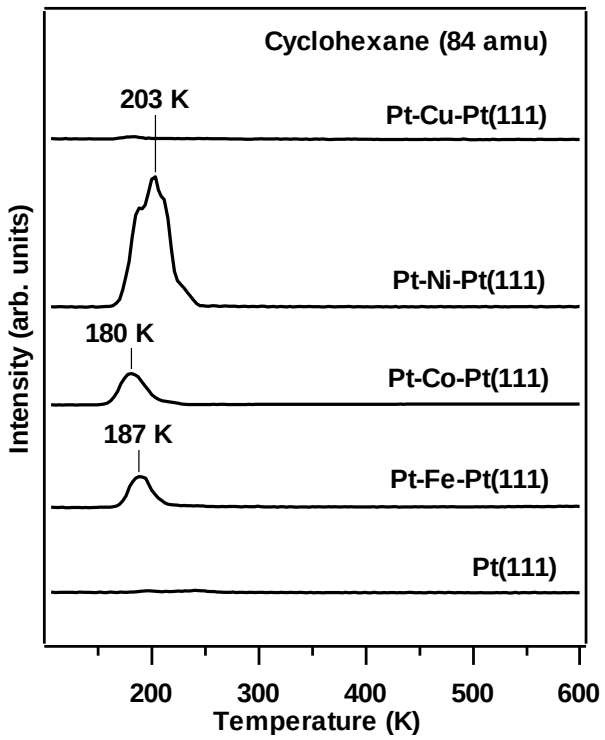
Low-Temperature Hydrogenation of Cyclohexene Due to Weakly Bonded H

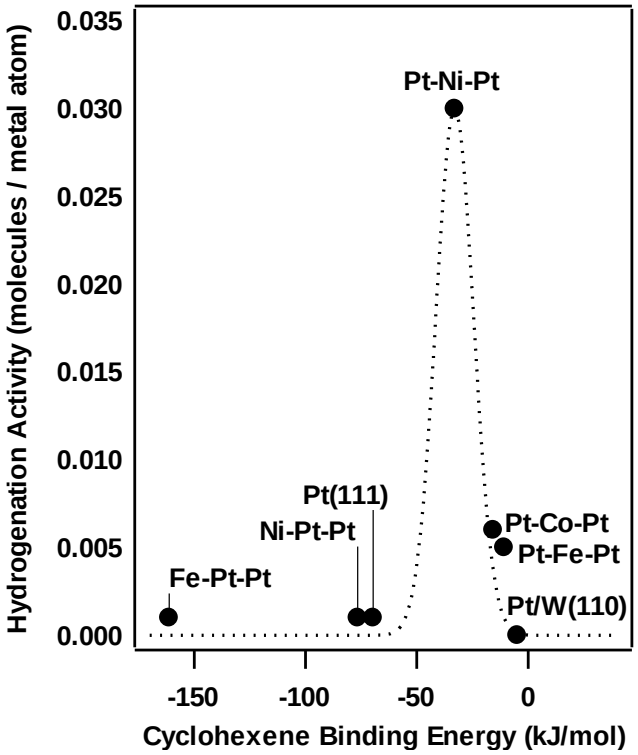




- Weakly bonded M-H leads to low-T hydrogenation

Binding Energies Correlate with Cyclohexene Hydrogenation Activity





Sabatier's principle: not too strong, not too weak!

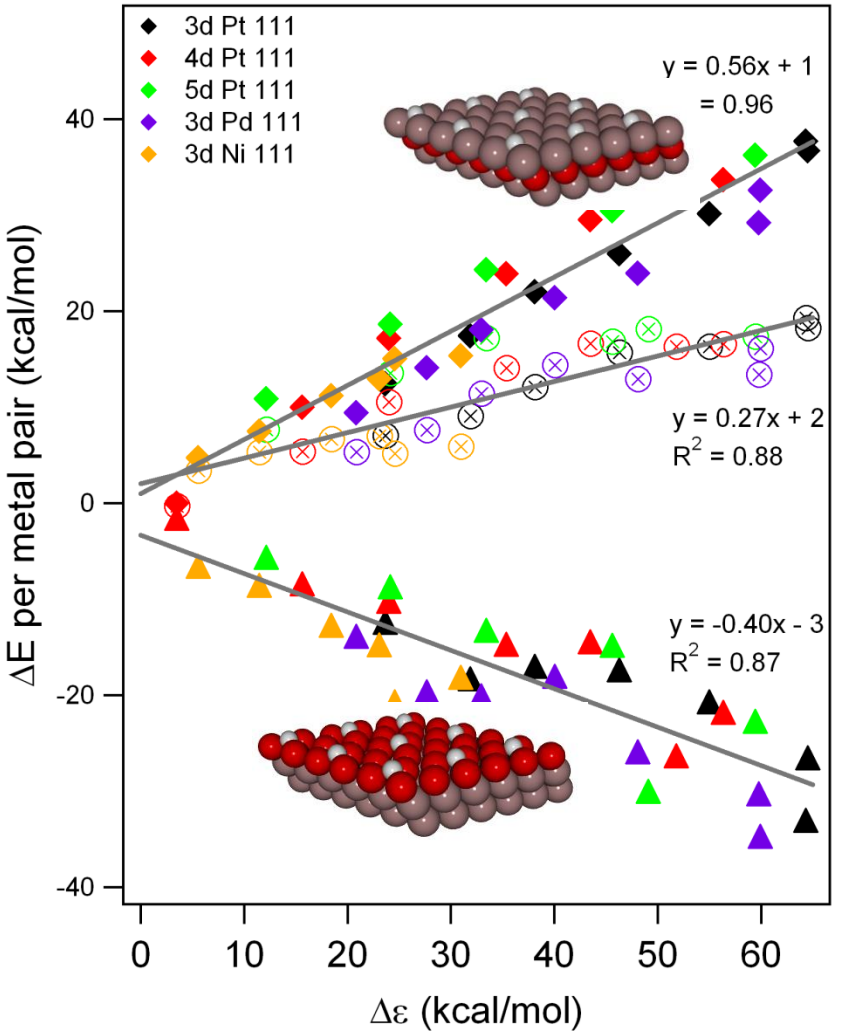
Volcano relationship allows prediction of hydrogenation activity

DFT Prediction of Stable Bimetallic Structures

General Stability includes:

- Admetals – 3d, 4d, 5d
- Host metals – Ni, Pd, Pt

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt



Vacuum

0.5 ML H

0.5 ML O

Menning & Chen,

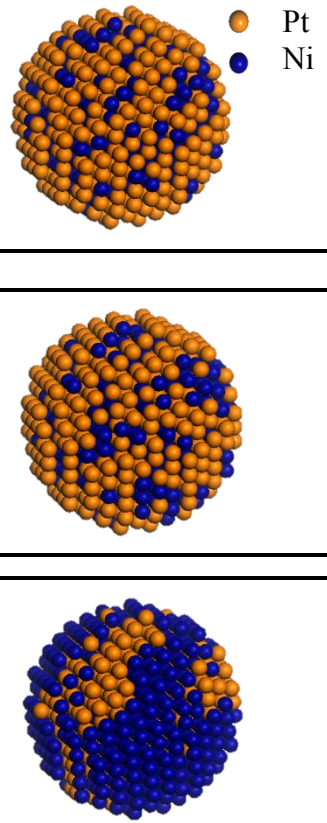
J. Chem. Phys, 130 (2009) 174709

Experimental Verification of Bimetallic Structures

Coordination Number	***10% H_2 at 50 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	1.9 ± 0.8	2.696 ± 0.003
Pt-Ni	3.5 ± 0.4	3.904 ± 0.007

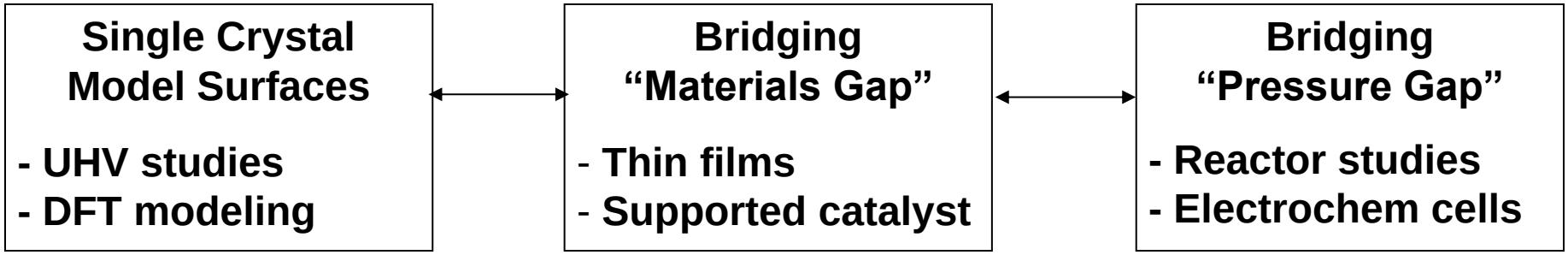
Coordination Number	***10% H_2 at 225 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	2.0 ± 0.7	2.675 ± 0.005
Pt-Ni	3.8 ± 0.3	4.148 ± 0.008

Coordination Number	***APR at 225 °C—NiPt/C***	
	Experimental	Simulation
Pt-Pt	6.0 ± 1.4	4.429 ± 0.006
Pt-Ni	1.9 ± 0.8	2.24 ± 0.03



Tupy, Karim, Vlachos, Chen, *ACS Catal*ysis, 2 (2012) 2290

Outline of Presentation



***Examples* of DFT prediction and experimental verification:**

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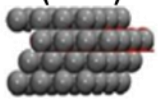
- Correlating hydrogen binding energy (HBE) with hydrogenation activity

- Correlating activation barrier with hydrogenation selectivity

Selective Hydrogenation Requires More Complicated DFT Calculations

Activation barriers on Pd(111) surface (eV):

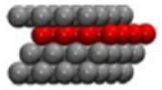
Pd(111)



$$C_4H_6 \underset{-H\ 0.64}{\overset{+H\ 1.04}{\rightleftharpoons}} C_4H_7 \underset{-H\ 0.49}{\overset{+H\ 0.92}{\rightleftharpoons}} C_4H_8 \underset{-H\ 0.49}{\overset{+H\ 1.01}{\rightleftharpoons}} C_4H_9 \underset{-H\ 1.05}{\overset{+H\ 0.87}{\rightleftharpoons}} C_4H_{10}$$

Activation barriers on PdNiPd(111) surface (eV):

PdNiPd(111)



$$C_4H_6 \underset{-H\ 0.60}{\overset{+H\ 0.68}{\rightleftharpoons}} C_4H_7 \underset{-H\ 1.03}{\overset{+H\ 0.88}{\rightleftharpoons}} C_4H_8 \underset{-H\ 0.81}{\overset{+H\ 0.88}{\rightleftharpoons}} C_4H_9 \underset{-H\ 1.52}{\overset{+H\ 0.80}{\rightleftharpoons}} C_4H_{10}$$

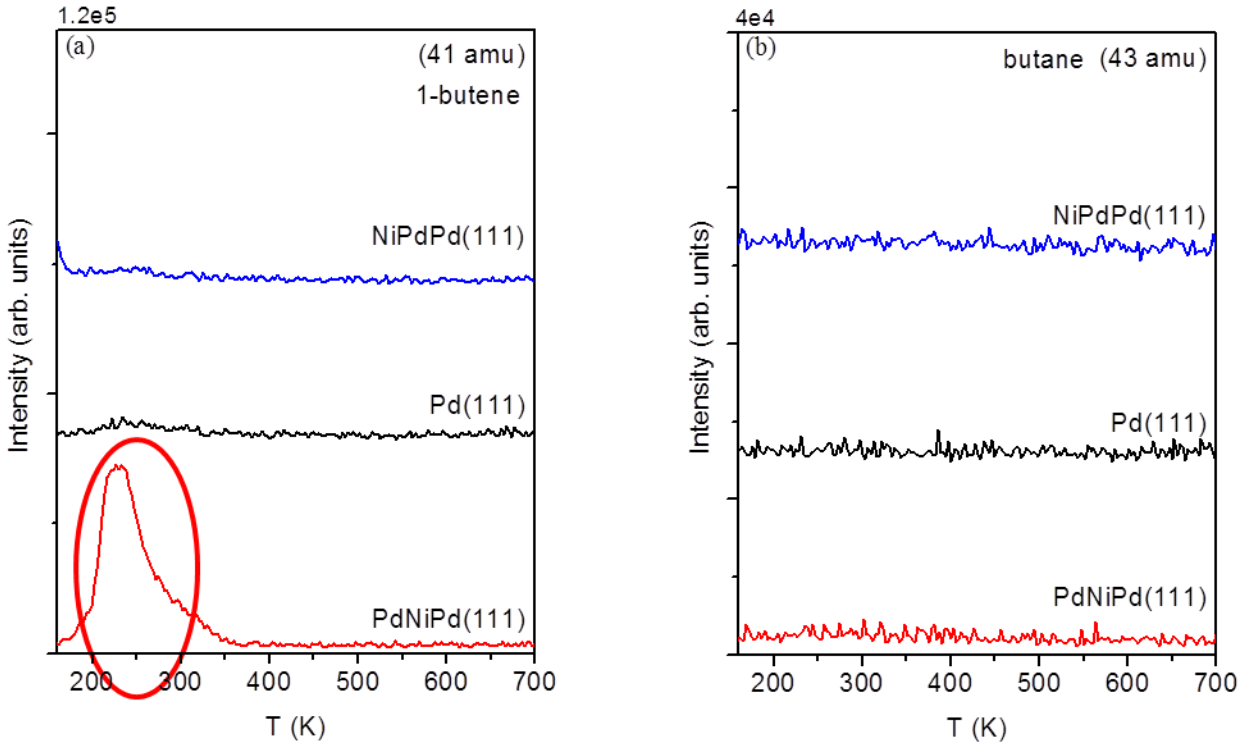
The activation barriers are generally lower on PdNiPd(111) than on Pd(111), leading to higher hydrogenation activity on PdNiPd(111)

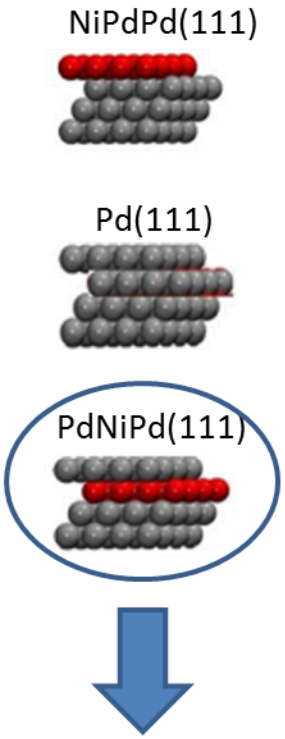
Predicting Selectivity Requires DFT Calculations of Reaction Network

Surface		Pd(111)	PdNiPd(111)
d-band center (eV)		-1.90	-2.25
Binding energy (kcal/mol)	C_4H_6	-34.47	-19.19
	C_4H_7	-37.27	-13.48
	C_4H_8	-12.68	-2.90
	C_4H_9	-36.54	-29.67
	C_4H_{10}	-2.61	-2.54

Binding energy of butene is weaker on PdNiPd(111), leading to higher selectivity for butene production on PdNiPd(111)

Experimental Verification on Model Surfaces



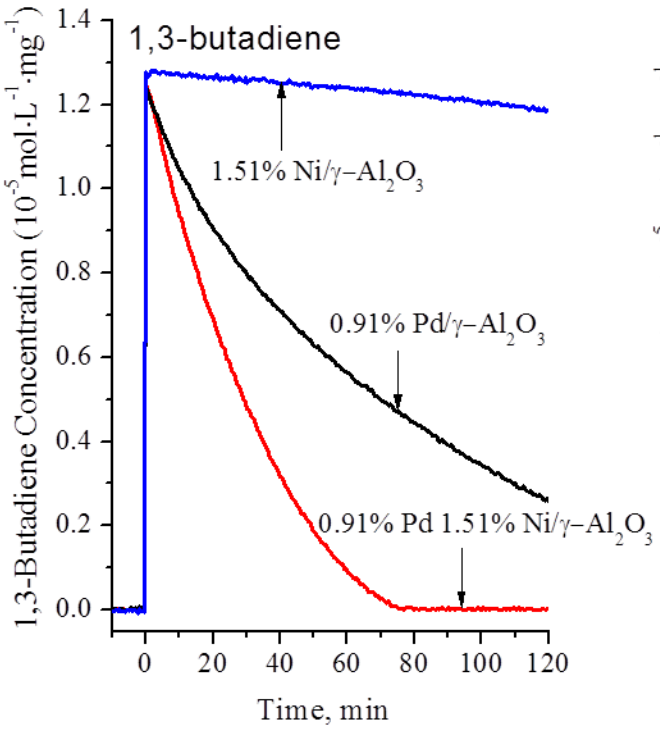


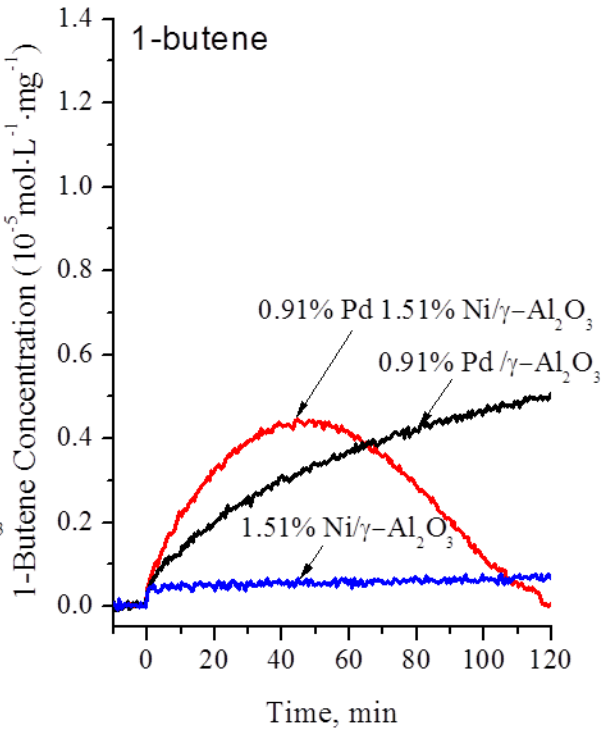
UHV-TPD: Ultra-High Vacuum Temperature Programmed Desorption

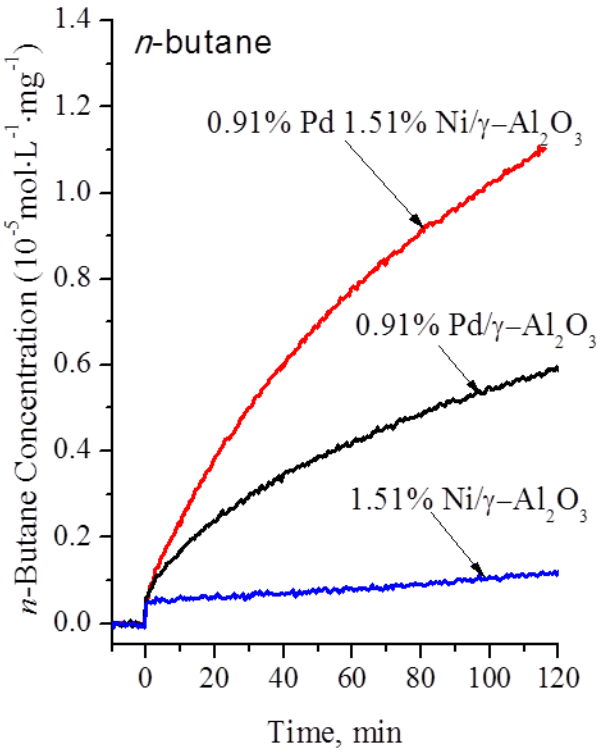
Stable bimetallic structure
under hydrogenation conditions

PdNiPd bimetallic structure is very active for 1,3-butadiene hydrogenation, and may also be selective for 1-butene production

Batch Reactor: Hydrogenation Activity

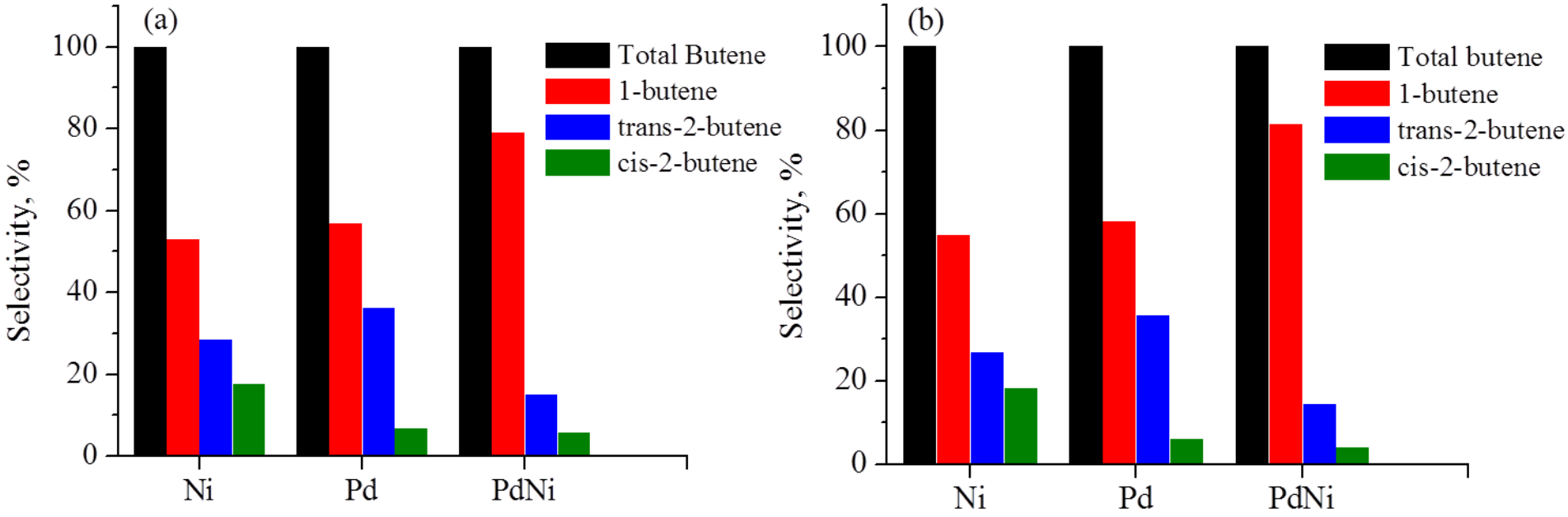






Activity trend: PdNi > Pd >> Ni

Flow Reactor: Hydrogenation Selectivity



Selectivities in flow reactor at conversions of (a) 10% (b) 60%

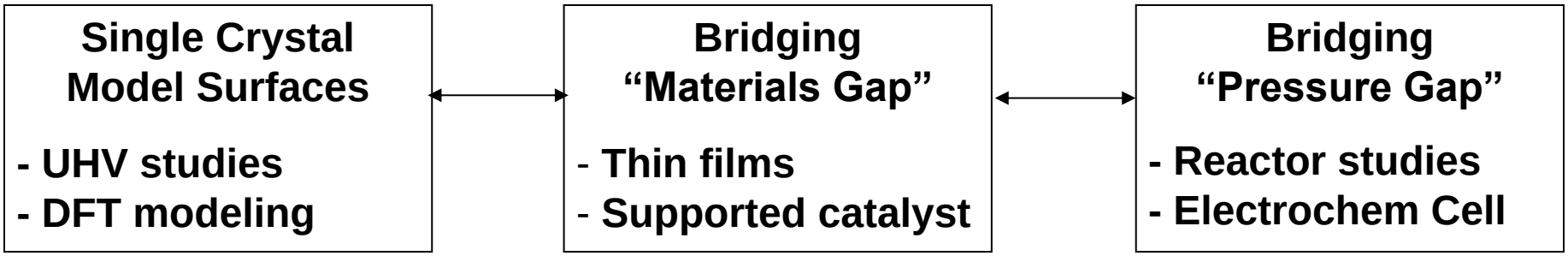
H_2:C_4H_6 = 2.2:1 Total Flow Rate: 9.6 ml/min

PdNi shows higher 1-butene selectivity than Pd, and higher yield in producing 1-butene

Hou, Porosoff, Chen & Wang, *J. Catalysis*, 316 (2014) 1

Conclusions

- Bimetallic and carbide catalysts offer the advantages of reduced cost and enhanced activity, selectivity and stability
- Combined theory, surface science, and catalytic studies are critical in design of novel catalytic materials



Review: Yu, Porosoff & Chen, "Review of Pt-based Bimetallic Catalysis: From Model Surfaces to Supported Catalysts", *Chemical Reviews*, 112 (2012) 5780